MICROSTRUCTURE AND PROPERTIES OF Mg-Nd-Zn-Zr ALLOYS

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ABSTRACT

One of the limitations of magnesium alloys is their low mechanical properties at elevated temperatures. In order to improve the creep strength, rare earth element neodymium Nd is added to Mg-0.3Zn-0.32Zr alloy. A significant grain refinement has already been achieved by the Zr addition in the base metal. The inclusion of Nd further reduces grain size from 120 μm to 75 μm. When the Nd content is less than 1%, the Nd is fully dissolved into Mg matrix. Increasing the Nd addition to 1.6% leads to a precipitation of $Mg_{12}Nd$ intermetallic phase at grain boundaries. The Nd-contained materials undergo a T6 heat treatment with a solution treatment at 530ºC for 8 hours followed by an aging at 250ºC for 12 hours. The heat treatment results in the Nd fully dissolved and then re-precipitated as $Mg_{12}Nd$, distributing as cluster within the grains and along the grain boundaries. These $Mg_{12}Nd$ precipitation significantly increases the mechanical properties of the materials, especially the high temperature properties. The 200ºC tensile strength is 120 MPa for 0.2% Nd-contained alloy and 200 MPa at 2.6% Nd. Even at a higher temperature, 300ºC, the Nd-contained alloys still retain significant strength, 60MPa for 0.2% Nd alloy and 110 MPa for 2.6% Nd alloy. The heat treatment also results in some grain coarsening, and Nd acts as effective barriers for the grain agglomeration.

1 INTRODUCTION

As the lightest materials among all the structural alloys magnesium alloys have great potential to be used in many structural applications. Each year magnesium alloys are finding new applications in the aerospace and automotive industry [1]. However, one of the limitations of magnesium alloys for structural applications is their low mechanical properties at elevated temperatures [2]. In order to improve their creep strength, rare earth (RE) and/or alkaline earth elements in small quantities have been effectively used as alloy additions [3-6]. Mg-RE alloys, as a group of speciality light alloys, they have found important applications in the aerospace, military, automotive and other industries, both as wrought alloys and sand or permanent mould cast alloys. Currently the Mg-RE system is the only magnesium alloys that can offer adequate creep resistance for application at temperatures above 200ºC [7]. Among them Mg-Nd alloy is particularly attractive because it can be effectively age strengthened by the precipitation of metastable Mg-Nd phases during aging treatment. A small amount of Zn is usually added to enhance the hardening ability of the alloy and Zr is added as a grain refiner. In this paper, rare earth element neodymium Nd is added to Mg-0.3Zn-0.32Zr alloy. The effects of Nd on the microstructures and mechanical properties at elevated temperature of the magnesium alloy are investigated.

2 EXPERIMENTAL PROCEDURES

The magnesium alloys were prepared in a boron nitride coated mild steel crucible, heated by an electrical resistance furnace. The starting materials were 99.9% Mg, 99.99% Zn, Mg-30%Nd master alloy and Mg-33.3%Zr master alloy. The mixtures were protected by RJ2 cover flux and Ar gas during melting. The magnesium ingot was melted in the steel crucible first, then pure Zn was added at 720ºC. Mg-Nd and Mg-Zr master alloys were added at 750ºC. After stirring the melt was held at 780ºC for 30 minutes to ensure the alloy elements were completely dissolved. RJ5 flux was used as refining agent to reduce the loss of Nd element. Following this procedure the melts were cast in a sand mould at a pouring temperature of 740ºC. The base alloy composition was selected to be Mg-0.30wt%Zn-0.32wt%Zr (Zr content is the soluble Zr). Nd content was varied by the addition of Mg-Nd master alloy and four Nd levels were investigated in this study. ICPS measurements indicated that the Nd contents were 0.21%, 0.84%, 1.62% and 2.65% respectively.

The castings were solution treated at 530 ± 5ºC for 8 hours, followed by aging treatment at 200 ± 5ºC for 12 hours. Tensile specimens with dimension of ∅15 × 100 mm were cut from the castings. Tensile tests at elevated temperature were carried out in Gleeble-1500D (Instron electronic universal materials testing machine). To observe the microstructure, small metallographic samples were cut from both as-cast and heat treated castings and mounted in cold-setting epoxy resin. All samples were ground initially with SiC paper down to 1200 grit grade, followed by polishing with 6 μm and 1 μm diamond suspensions and finally with UPS colloidal silica suspension. The samples were etched by Acetic-picral etchant (5 ml acetic acid, 4.2 g picric acid, 10 ml H2O and 50 ml ethanol). The grain structure of the samples was examined and photographed using a Reichert-Jung Polyvar optical microscope. Grain size measurement was carried out on the photographs using lineal intercept method in accordance with ASTM standard E112-96. The phases in the specimens were identified by means of X-ray diffractometer. The fractured surface morphology was examined by SEM (FEI Sirion).

3 RESULTS

3.1 The effect of Zr on grain size of Mg-Nd-Zn alloys

Zirconium is a potent grain refiner for magnesium alloys that contain little (impurity level) or no Al, Mn, Si, Fe, Ni, Co, Sn and Sb (zirconium forms stable and high melt-point compounds with these elements) [1]. The maximum solubility of Zr in molten magnesium is approximated 0.6%. The exceptional grain-refining ability makes Zr an important alloying element for magnesium alloys containing zinc, rare earths, thorium, calcium, or a combination of these elements.

The effect of Zr on grain size in Mg-Nd-Zn alloy is shown in Fig. 1, where the microstructures of Mg-2.65%Nd-0.30%Zn alloy with and without Zr addition can be observed. Zr addition results in a significant decrease in grain size of Mg-Nd-Zn alloy and without zirconium addition, the microstructure consists of coarse equiaxed grains. At a Zr level of 0.32%, the morphology transits to distinct hexagonal globular grains with a dramatic reduction in grain size. It can be seen that the zirconium addition produces a significant effect on both grain morphology and grain size to Mg-Nd-Zn alloys.

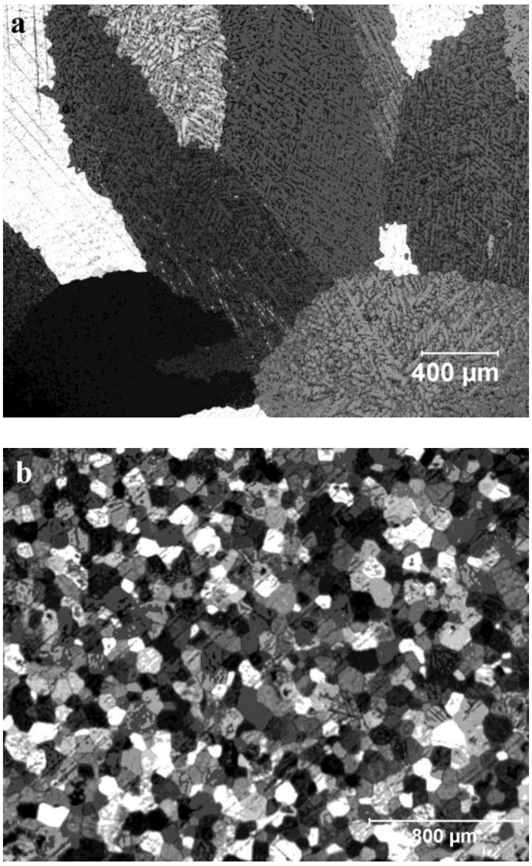

Fig. 1. Effect of Zr on the as-cast Mg-2.65Nd-0.30Zn alloy. (a) without Zr addition; (b) 0.32% Zr addition.

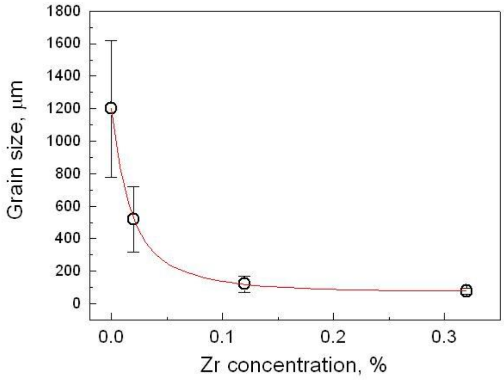

Fig. 2. Grain size as a function of soluble Zr concentration.

With different levels of Zr addition, Fig. 2 shows the average grain size of the materials plotted against soluble zirconium contents. As the soluble Zr content increases, grain size decreases very rapidly at the beginning. The initial 0.02% of Zr addition reduces the grain size from 1200 μm to 500 μm. When the Zr level reaches 0.05%, further addition of Zr produces a much more moderate reduction in grain size. The increase of the Zr level from 0.12% to 0.32% results in a grain size change only from 120 μm to 80 μm.

The mechanism of grain refinement of zirconium in magnesium has not been well determined yet [1]. Zr has the same h.c.p microstructure as magnesium and the lattice parameters of hexagonal zirconium (α=0.323nm and c=0.514nm) are very close to those of magnesium (α=0.320nm and c=0.52nm). Based on this, it is believed that zirconium particles may act as powerful nuclei for magnesium [8].

3.2 The effect of Nd on grain size and microstructure of as-cast Mg-Zn-Zr alloys

The effects of Nd addition on morphology and grain size of Mg-Zn-Zr alloys are shown in Fig. 3 and Fig. 4. The soluble Zr concentration is kept at 0.32%, which will lead to improved grain refinement as indicated in Section 3.1. Nd addition has an especially obvious effect on grain morphology and also has an effect, though less significant, on grain size. For the alloys with 0.21% and 0.84% Nd additions, the grain morphology is typical hexagonal globular, as shown in Fig. 3a and b. As the Nd addition increases to 1.62% and 2.65%, grain morphology changes to some extent of rosette-like structure, as shown in Fig. 3c and d. The grain size vs. Nd addition is plotted in Fig. 4, and as seen the Nd addition results in the decrease of grain size from 120 μm at 0.21% Nd to 78 μm at 2.65% Nd.

3.3 The effect of heat treatment on microstructure

Castings of Mg-Nd-Zn-Zr alloys with different Nd levels but constant Zr (0.32%) and Zn (0.30%) were

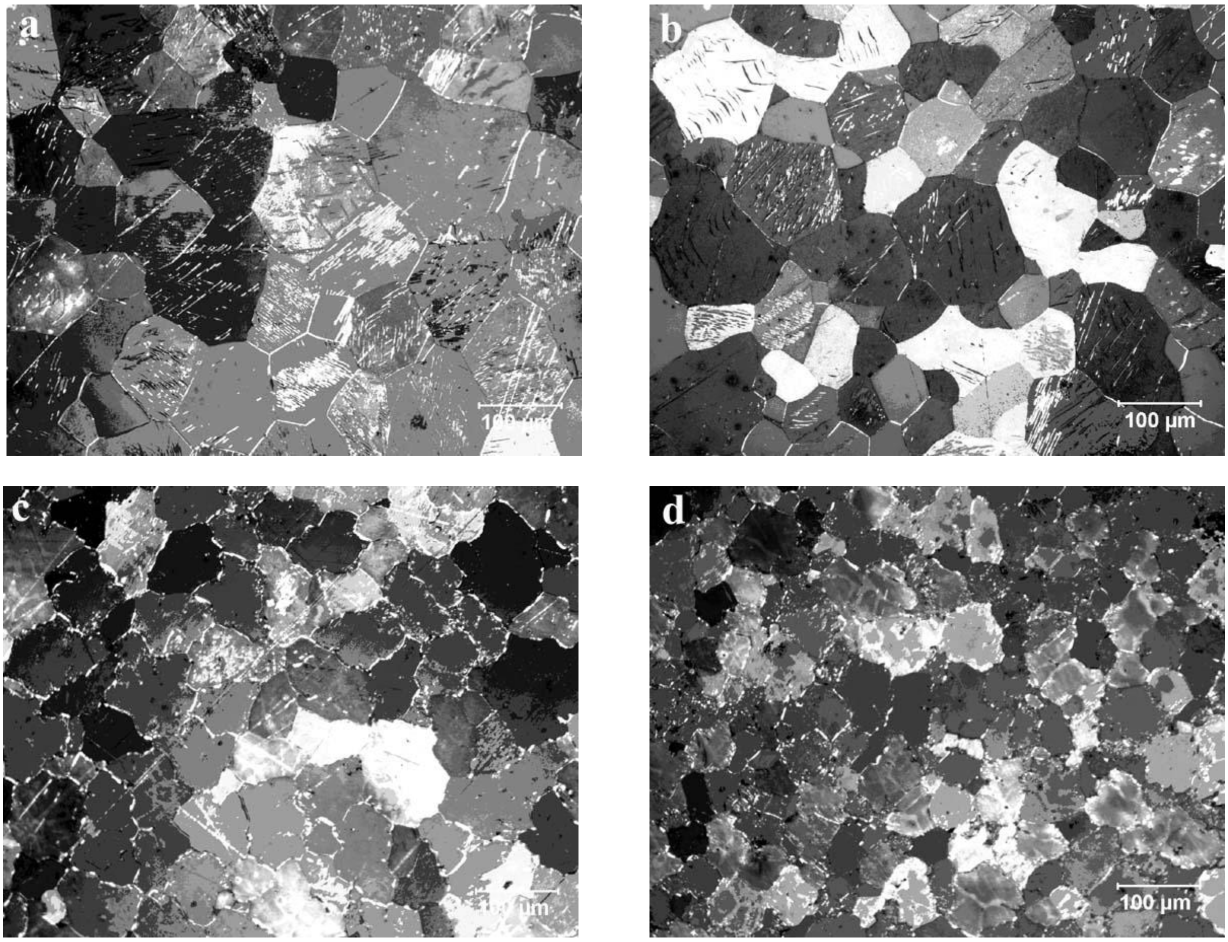

Fig. 3. The effect of Nd on as-cast morphology of Mg-Zn-Zr alloys, (a) 0.21% Nd; (b) 0.84% Nd; (c) 1.62% Nd and (d) 2.65% Nd.

made. Solution treatment was carried out on the samples at 530ºC for 8 hours followed by aging at 250ºC for 12 hours. The microstructures of the heat treated samples are shown in Fig. 5. For the alloys with low Nd concentration, the solution and aging treatments do not have much effect on grain morphology, which is still hexagonal globular, compared with Fig. 3. However, an obvious increase in grain size is observed. For the 0.21% Nd alloy, its grain size increases from 120 μm to

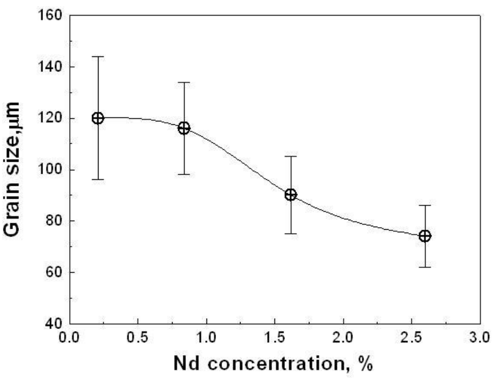

Fig. 4. Grain size of Mg-Zn-Zr alloys as a function of Nd addition.

175 μm, while for high Nd concentration (over 1.6%) alloys, the initial rosette-like grain morphology changes to perfectly defined hexagonal globular with slight increase in grain size. The change of the grain size with Nd addition is shown in Fig. 6.

3.4 The effect of Nd on mechanical properties at elevated temperatures

The mechanical properties at elevated temperatures up to 300ºC can be seen in Fig. 7. The effect of temperatures below 200ºC on mechanical properties is not significant. When the test temperature increases to 250ºC, there is an obvious decrease in tensile strength and yield strength, further increasing to 300ºC results in a halving of the strength when compared to the nominal strength.

The tensile strength and yield strength of Mg-Nd-Zn-Zr alloys increase constantly with the increase of Nd addition and it is important to note that the strength improvement is more significant at high levels of addition. The improvement of mechanical properties is contributed to the precipitation of $Mg_{12}Nd$ intermetallic phase in grain boundaries and within grains. It should be pointed out that the temperature range between 150 - 200ºC is the working temperature for automotive

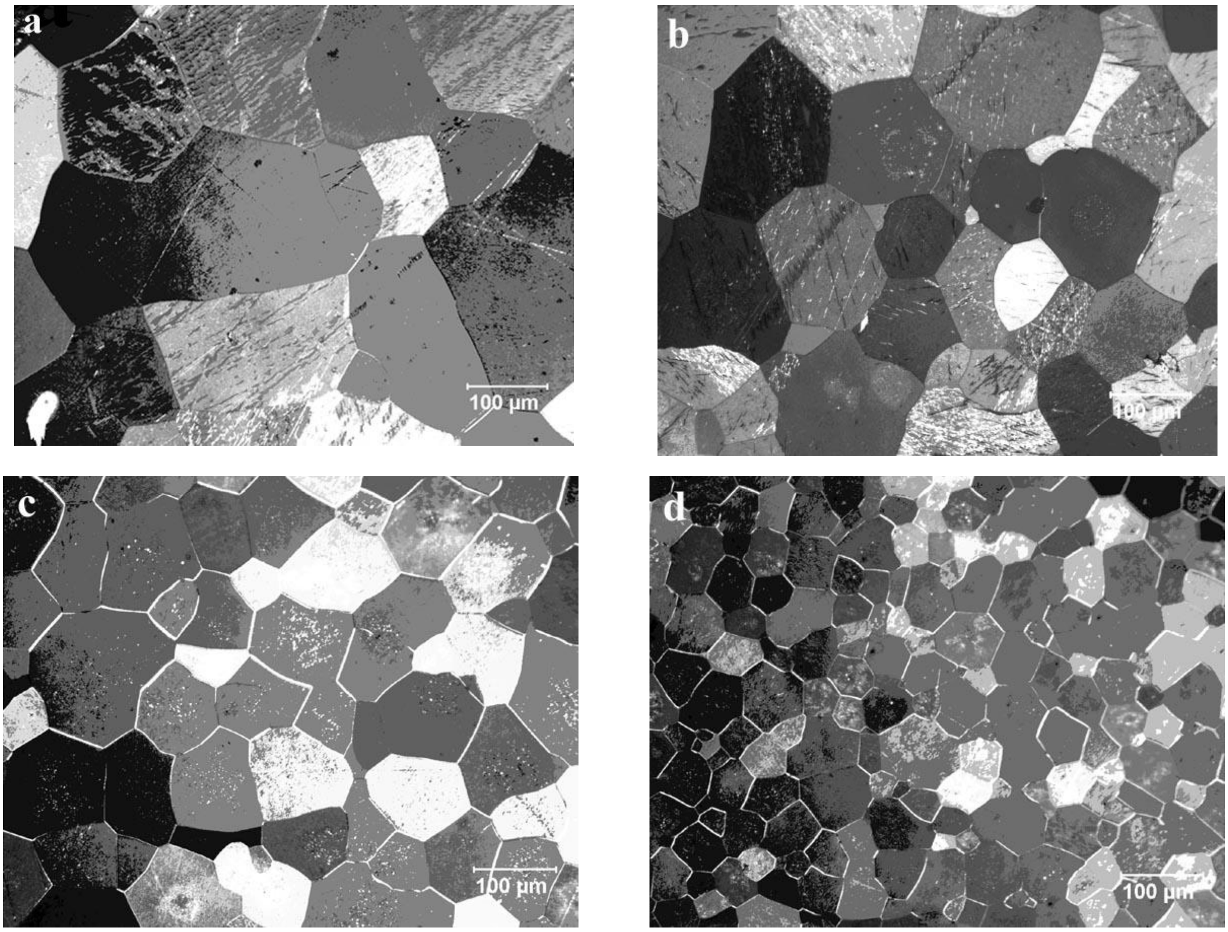

Fig. 5. The effect of Nd on microstructure of Mg-Nd-Zn-Zr alloy after solution and aging treatment, (a) 0.21% Nd; (b) 0.84% Nd; (c) 1.62% Nd and (d) 2.65% Nd.

powertrain components. For example, the transmission case has operating temperature up to 175ºC and engine block is up to 200ºC [3]. Our results show that alloys containing medium Nd addition (1.6%) have already possessed very high mechanical properties. Compared with the commercial creep resistant alloys, such as the commonly used ML10, which contains high Nd addition (2.2-2.8%), the Mg-1.6Nd-0.3Zn-0.32Zr has comparable mechanical strength but much lower cost due to the replacement Nd by less expensive Zr.

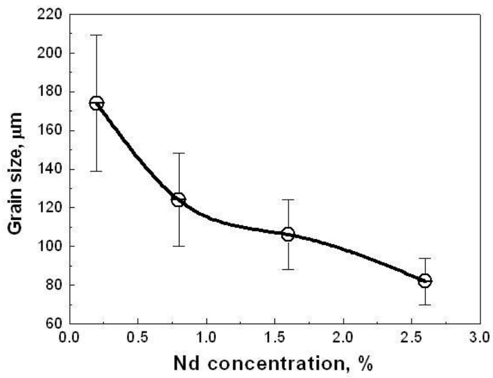

Fig. 6. Grain size of Mg-Nd-Zn-Zr alloys as a function of Nd addition.

SEM observation of fracture surface of Mg-Nd-Zn-Zr alloys is shown to have mixed fracture types. The fractures are in a mixed manner. For the samples tested below 200ºC, cleavage fracture is the dominant mechanism accompanied with a small quantity of elongated dimples, while for the samples tested above 250ºC, the fractures are typical dimple fracture, as seen in Fig. 8.

4 DISCUSSION

It is well know that grain boundary plays a critical role in creep. Fine grain structure is desirable as it will assist with achieving creep resistance. When examined the effect of various solute element addition on grain size of Mg alloy can be estimated by using the following Growth Restriction Factor defined as [9]:

$$GRF = m\,(k-1) \tag{1}$$

where m is the slope of liquidus line and k is the equilibrium solute distribution coefficient. *GRF* value of various alloying elements in magnesium is calculated and shown in Table 1. The calculation is based on one unit of concentration in order to compare the effectiveness of different alloy additions on grain refinement.

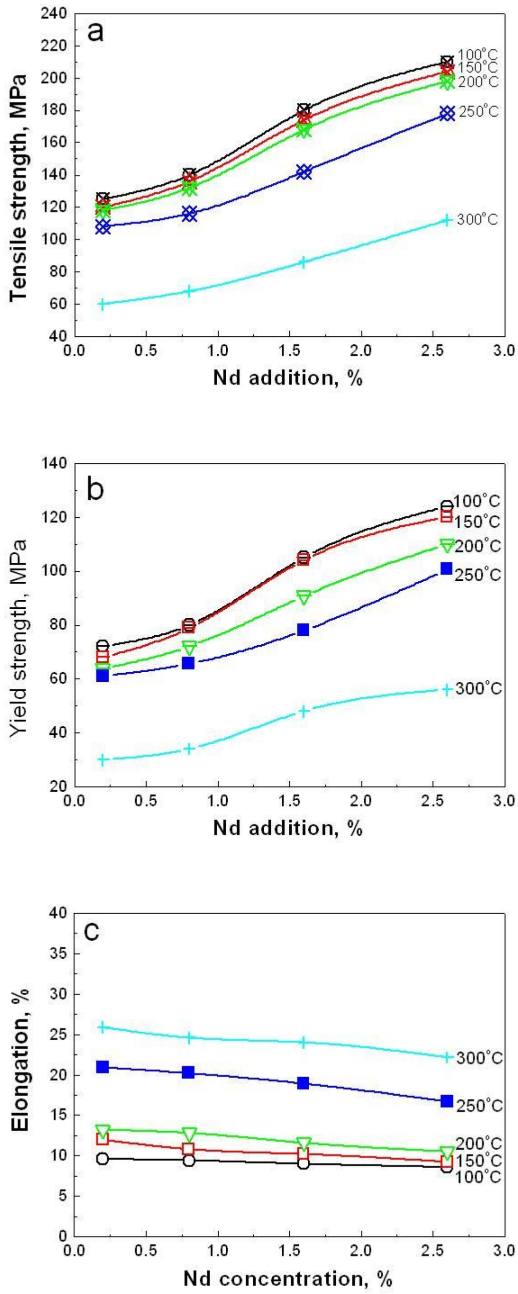

Fig. 7. Tensile properties of Mg-Nd-Zn-Zr alloys at elevated temperatures. (a) tensile strength; (b) yield strength and (c) elongation.

Table 1. m, k and GRF of various alloying elements in magnesium [9] .

Elements	*m*	*k*	*GRF*
Zr	6.9	6.6	38.3
Nd	-3.0	0.1	2.8
Ce	-2.9	0.04	2.7
Y	-3.4	0.5	1.7

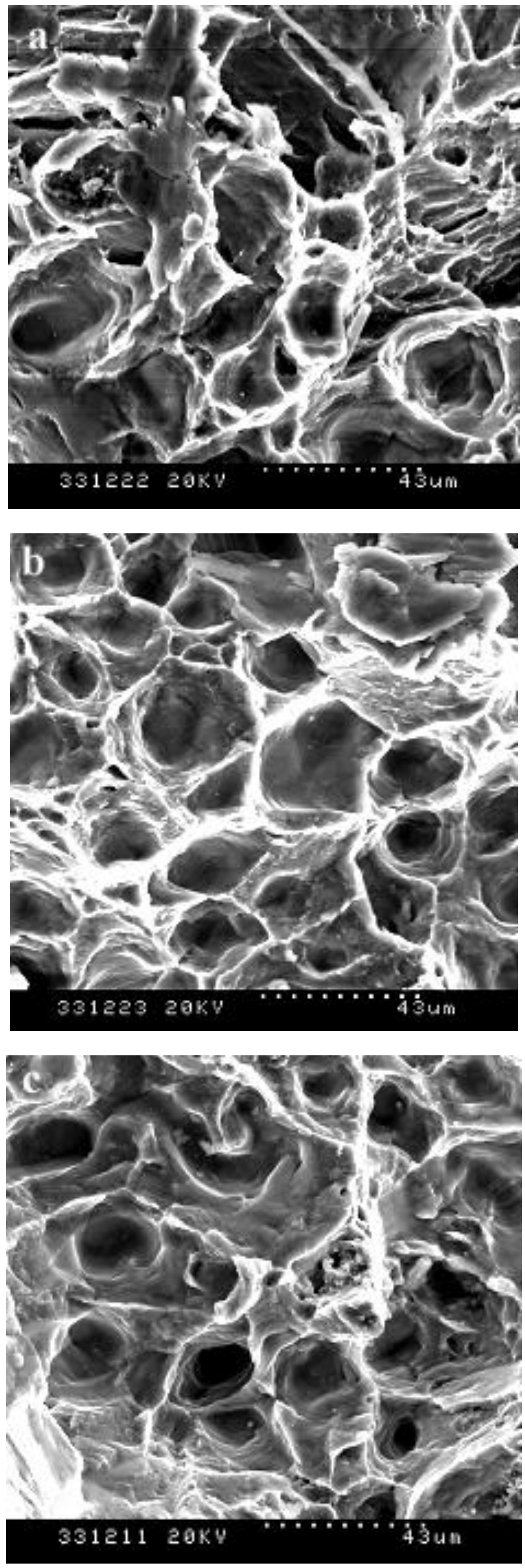

Fig. 8. Fracture surfaces of Mg-Nd-Zn-Zr alloys tested at 250ºC. (a) 0.21%Nd; (b) 1.62%Nd and (c) 2.65%Nd.

Zr has the highest GRF value, 38.3. Other commonly used alloy elements in RE-Mg alloys, such as Nd and Ce, are one order of magnitude lower, 2.7. The GRF value of Y is only 1.7. Therefore Zr is much more powerful in terms of grain refinement in the non-Al containing Mg alloys. This has been confirmed by comparison of Fig. 1 and Fig. 3.

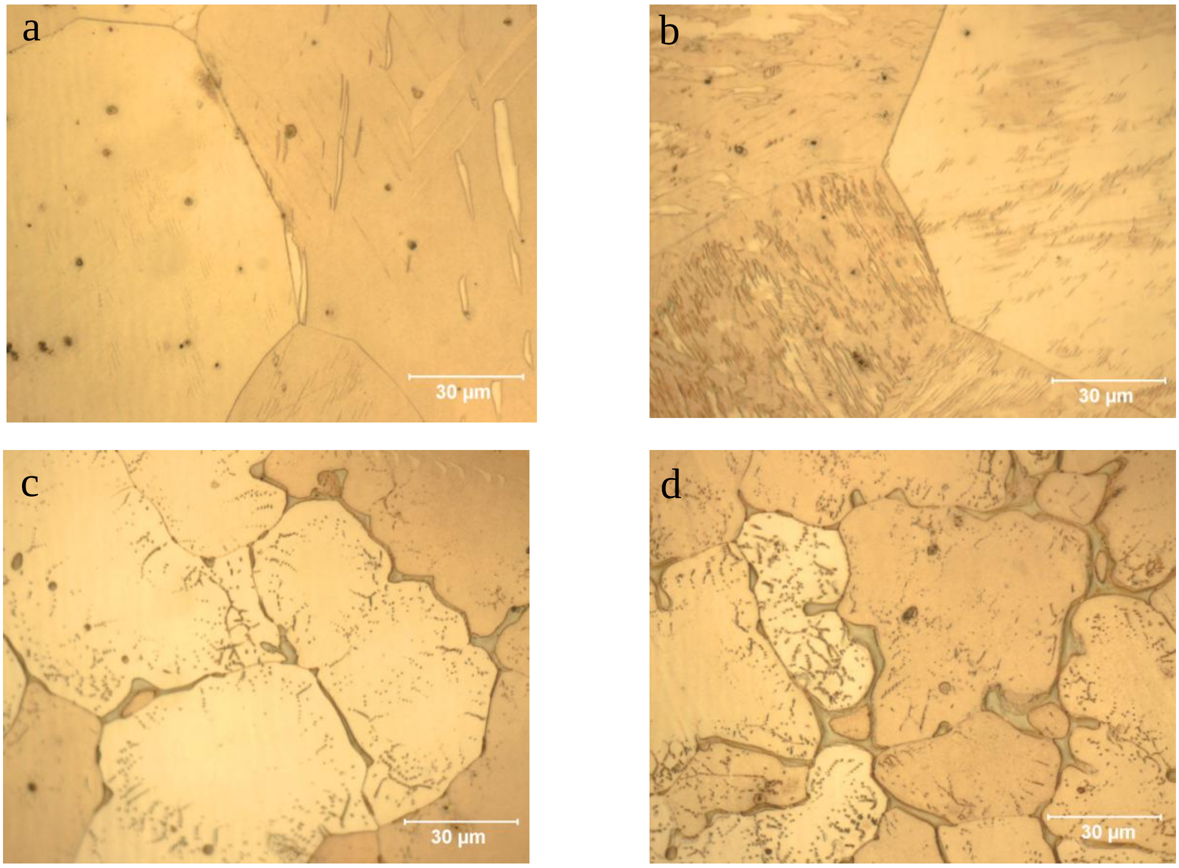

Fig. 9. Grain boundaries of as-cast Mg-Nd-Zn-Zr alloys, where $Mg_{12}Nd$ precipitates when the Nd addition is high. (a) 0.21% Nd; (b) 0.84% Nd; (c) 1.62% Nd and (d) 2.65% Nd.

When the addition is lower than 0.8%, solute elements Nd and Zn are all dissolved into the Mg matrix and no intermetallic precipitate appear in grain boundaries. With Nd addition increased to 1.6%, there are obvious precipitates in the grain boundaries, as shown in Fig. 9. According to the equilibrium phase, the maximum solubility of Nd in Mg is 3.6%. However under the cooling condition used in this experiment, intermetallics can be formed and preferentially precipitated in grain boundaries even though the Nd addition is far lower than its maximum solubility in Mg matrix. XRD spectrum and EDS analysis indicate that the intermetallics are $Mg_{12}Nd$ with no Zn content. The Zn addition is relatively low in this study and it is most likely fully dissolved in Mg matrix.

The alloy addition of Nd plays an important role of preventing the grain growth during solution treatment. The initially formed $Mg_{12}Nd$ is completely dissolved into the Mg matrix during the solution treatment, and then re-precipitated from the matrix as much finer clusters and non-uniformly distributed within grains and along grain boundaries, as shown in Fig. 10. These clusters act as effective barrier for grain amalgamating during the heat treatment, which is carried out for a long period of time. The low Nd addition alloy (0.21%) shows a grain growth from 120 µm to 175 µm after the heat treatment, due to the absence of such barriers. While the other higher Nd addition alloys only see a very moderate increase in grain size. The material's

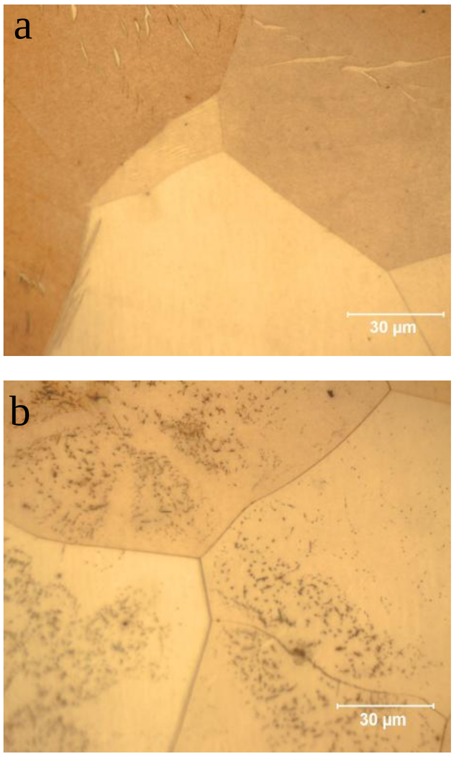

Fig. 10. Grain strictures of heat treated Mg-Nd-Zn-Zr alloys, showing no $Mg_{12}Nd$ precipitation when Nd addition is low (a), 0.84% Nd; while at 1.6% Nd, $Mg_{12}Nd$ clusters are within the grains and at grain boundaries (b).

higher strength at elevated temperatures for the high Nd-containing alloys is attributed to two factors: (a) Nd addition results in fine grain structure and more grain boundaries; (b) excessive Nd precipitates as $Mg_{12}Nd$ cluster within grains and along grain boundaries. The Nd-containing clusters act to help lock the grain boundaries and reduce grain boundary sliding.

5 CONCLUSIONS

1. Nd addition has significant effect on both grain size and grain morphology in Mg-Nd-Zn-Zr alloys. Increasing Nd from 0.21% to 2.65%, the grain size is reduced from 120 μm to 76 μm, and the grain morphology is changed from hexagonal to rosette-like to some extent. For the alloys containing more than 1.60% Nd, the intermetalitics $Mg_{12}Nd$ phase exists in grain boundaries and at triple points of grain boundaries.

2. After solution and aging heat treatments, $Mg_{12}Nd$ phase disperses in the matrix and grain boundaries, which helps to lock the grain boundaries and reduce grain boundary sliding. Consequently the material's strengths at elevated temperatures have been significantly improved by the Nd addition.

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